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Anelasticity of nitrogen in α-iron

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With 2 figures in the text

In two previous papers by Borelius and Åström (1), and Åström (2), some measurements on the anelasticity of nitrogen in iron have been reported. The measurements were carried out with a relaxation method which differed in several respects from the torsional pendulum method commonly used for the study of the internal friction. Using this relaxation method, it was found that, at −18°C, the dependence of the elastic after-effect on the concentration of solute nitrogen was non-linear. This was thought to be due to an interaction between the nitrogen atoms. Considering only an interaction in pairs and assuming that these pairs do not take part in the relaxation process, an approximate formula was derived from statistical considerations for the dependence of the after-effect on the nitrogen content

$$\frac{\varepsilon_2}{\varepsilon_1} = k \cdot \frac{p}{1 + \frac{4}{3} p \cdot e^{\frac{E}{RT}}} \tag{1}$$

where $\varepsilon_2/\varepsilon_1$ is a measure of the elastic after-effect, p the ratio of N to Fe, E the energy of dissociation, and k a constant of proportionality which may depend on the temperature and the dimensions and orientations of the crystals in the sample.* Fitting eq. (1) to the experimental values gave $E = 2\,600$ cal/mole and $k = 51$.

Since the appearance of these papers, accurate determinations of the internal friction of nitrogen in iron using the torsional pendulum method have been reported by Fast and Verrijp (3) and Rawlings and Tambini (4). These measurements gave, within the limits of accuracy, a linear relation between the internal friction and the concentration of nitrogen. The values obtained for the internal friction were, at the highest concentrations, about 25 % above those of our measurements. The discrepancy between the results of the two methods was said to be due to a precipitation, in our case, of the solute nitrogen before the anelasticity was measured. Since the results of the pendulum method were obtained at room temperature, this suggested a recalculation of our results to this temperature by means of eq. (1). It was then found that the influence of temperature according to eq. (1) accounted for most of the discrepancy. In the present paper the results of some new measurements, which give further evidence for the existence of such a temperature effect, will be reported.

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* In paper (2) eqs. (6), (7), and (9), the dissociation energy was given with negative sign which is less convenient.

The method used was the same as that employed in the earlier measurements. The result of a series of measurements on a sample containing 0.095 wt% of nitrogen are shown in fig. 1. The after-effect was determined at -12°, -24°, and -29°C without any renewed heat treatment of the sample. For a qualitative study of the temperature effect on the elastic after-effect, any precipitation occurring during the quenching or the mounting af the samples is only of secondary importance. It is, however, necessary to consider a possible precipitation during the relaxation measurements since it took a rather long time to perform the measurements at the different temperatures due to the large heat capacity of the relaxation equipment. The author has therefore determined the change of the after-effect at -24°C with time after the quenching. Assuming that the rate of precipitation does not change markedly during the intervening measurements at -12° and -29°, the curve through the points in fig. 1 obtained at -24° can be assumed to describe approximately the change in the after-effect due to the precipitation. By means of this curve it is possible to compare the results at -12° and -29° with the corresponding values at -24°. It is at once obvious that the elastic after-effect is temperature-dependent and that this effect appears, at least qualitatively, in the way predicted by eq. (1). The after-effects at -12° and -29° relative to -24° have been estimated by eq. (1) and are plotted in the figure.

Some new measurements have also been made on the dependence of the after-effect on the concentration of solute nitrogen. Special care was taken to eliminate or reduce the influence of precipitation. Precipitation may occur both during the quenching and the mounting of the samples and also during the relaxation measurements. In the quenching procedure used here, the spirals with known nitrogen contents were quenched from a temperature at which all the nitrogen was in solution, by dropping them directly into a 20 % solution of caustic soda in water. Since the contact area between the sample and the cooling medium was large the quenching was rapid in spite of the relatively large mass of the sample. The time necessary for the mounting in the relaxation apparatus was 3–5 minutes. During the mounting the sample was at about room temperature but, within ten minutes after quenching, the temperature was definitely below zero. The precipitate which appears at these temperatures is the metastable iron-nitride. The curve in fig. 1 gives the rate of precipitation of this phase at -24°. The shape of the curve is almost exponential with a time constant of about 130 hours. Calorimetric measurements on the metastable phase at 130°C (2) have given a time constant for the precipitation of about 0.1 hour. From these results it is obvious that a few minutes at room temperature during the mounting will have only a very small effect on the precipitation. In order to correct for the amount of precipitation occurring during the relaxation measurements, the author determined the change of the after-effect with time as in fig. 1 and extrapolated the curves to zero time. Only at the highest concentrations the rate of precipitation was so high that it made corrections of the measured after-effects necessary.

The new measurements on the dependence of the elastic after-effect on concentration, made at -18° as in the previous measurements, gave within the limits of error the same values for the after-effect as before for nitrogen concentrations less than about 0.05 wt%. However, at higher concentrations, the new

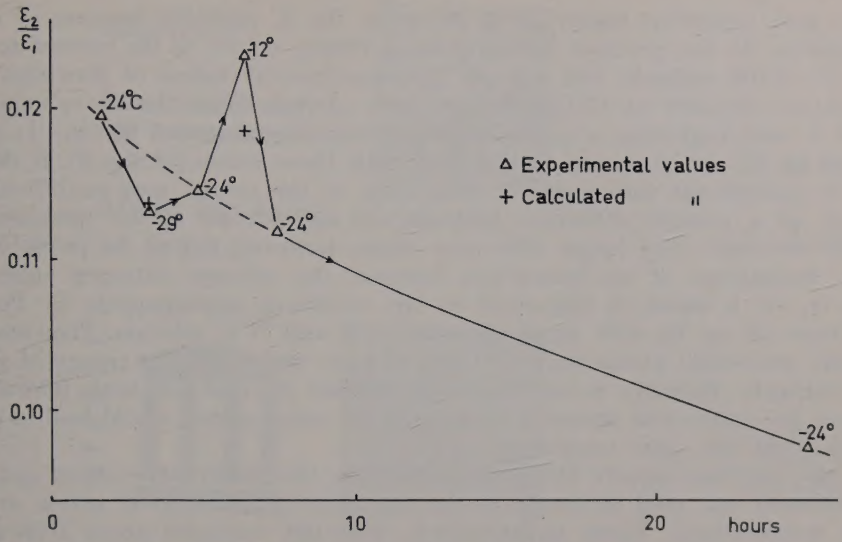

Fig. 1. Elastic after-effect versus time after the quenching for a specimen containing 0.095 wt % nitrogen.

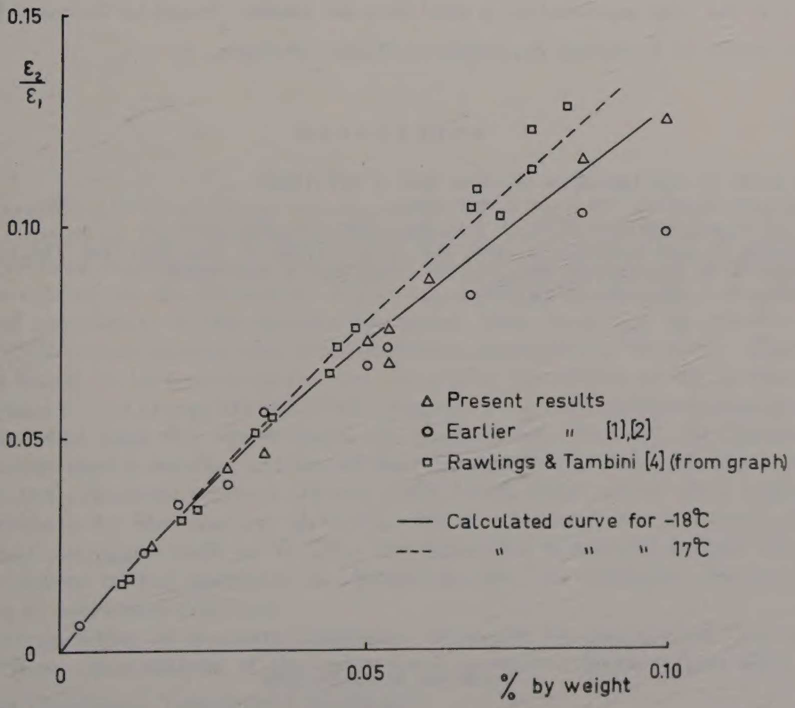

Fig. 2. Elastic after-effect versus concentration of solute nitrogen.

values were somewhat higher, as is shown in fig. 2, probably because of some precipitation in the previous measurements. Fitting eq. (1) to the present results gives $E = 2\,100$ cal/mole and $k = 43$. The experimental values of Rawlings and Tambini (4) obtained at 17°C have also been plotted. With the above values of E and k (and neglecting a possible temperature dependence of k), eq. (1) gives a curve at 17° which agrees within 10% with these values (cf. fig. 2). It should here be pointed out that a direct comparison of the results may be difficult on account of a possible difference in grain size and texture of the specimens of the two methods. Any larger difference seems, however, not to be probable.

The assumption of an interaction between the adjacent nitrogen atoms on which eq. (1) is based, is supported by the results of measurements by Powers and Doyle (5) on Ta with small amounts of O and N in solution. They showed that the interstitial atoms tend to unite in pairs with a binding energy of about 2 000 cal/mole. Recently it was shown by Fischer (6) that an elastic interaction between the interstitial atoms in body-centered cubic metals would lead to energies of about the same magnitude.

In our previous reports the relation between the elastic after-effect and the concentration was used to determine the solubility of nitrogen in α-iron at different temperatures. These measurements were not extended above 0.05 wt %. The corrections of the calibration curve at the highest concentrations, according to fig. 2, will therefore not change the solubility thus obtained, within the limits of error of the measurements.

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REFERENCES

1. ÅSTRÖM, H. U. and BORELIUS, G., Acta Met. *2*, 547 (1954).
2. ÅSTRÖM, H. U., Arkiv för Fysik *8*, 495 (1954).
3. FAST, J. D. and VERRIJP, M. B., J. Iron Steel Inst. *180*, 337 (1955).
4. RAWLINGS, R. and TAMBINI, D., Acta Met. *3*, 212 (1955); J. Iron Steel Inst. *184*, 302 (1956).
5. POWERS, R. W. and DOYLE, MARGARET V., Acta Met. *4*, 233 (1956).
6. FISCHER, J. C., Acta Met. *6*, 13 (1958).

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